

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 1 Sept 2006		2. REPORT TYPE Final Technical Report		3. DATES COVERED (From - To) 1 Sept 2006-1 Sept 2007	
4. TITLE AND SUBTITLE Programmable Triplet Formation and Decay in Metal Organic Chronophers				5a. CONTRACT NUMBER FA9550-05-1-0276	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
				5d. PROJECT NUMBER	
6. AUTHOR(S) Prof. Felix N. Castellano				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Bowling Green State University Bowling Green, Ohio 43403 T				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) SS(ES) USAF/AFRL AFOSR 875 North Randolph Street Arlington VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
				11. SPONSORING/MONITORING AFRL-OSR-VA-TR-2013-0919	
12. DISTRIBUTION AVAILABILITY STATEMENT Distribution Statement A: Approved for public release. Distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This proposal is primarily concerned with the design, synthesis, and photophysical characterization of photochemically stable metal-organic chromophores with low-lying triplet excited states, intended to possess systematically variable excited state absorption and emission properties. The main project theme is to investigate alternate pathways to populate long-lived excited triplet states of interest for Air Force applications including power limiting, ultrafast switching, remote identification, and solution-based photon up conversion processes. In many instances, metal-to-ligand charge transfer (MLCT) excited states are used to internally sensitize the formation of excited triplet states localized on the appended "organic" system with visible light. Progress has been made in all proposed project areas over the past year's funding period.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Unclassified	18. NUMBER OF PAGES 11	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (703)

**PROGRAMMABLE TRIPLET FORMATION AND DECAY IN
METAL-ORGANIC CHROMOPHORES**

Performance Report
September 1, 2006

AFOSR FA9550-05-1-0276

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Reporting Period:

September 1, 2005 – August 31, 2006

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2. OBJECTIVES

The project objectives are the same as originally proposed.

3. STATUS OF EFFORT

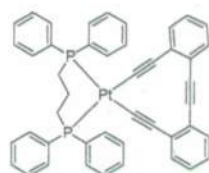
In the initial period of AFOSR support, significant progress has been made in several research project areas. A number of new Pt(II) MLCT complexes with and without various triplet energy acceptors have been prepared and in all cases their photophysical properties have been evaluated. Some of these materials show promise as optical power limiters exhibiting ultrafast response times to incident laser irradiation and large triplet-to-triplet excited state absorptions. In particular, we have developed an improved understanding of the nature of the absorption transients observed in platinum(II) terpyridyl acetylides. A promising new class of strongly luminescent Pt(II) charge transfer chromophores based on metallacyclic diacetylide structures have been introduced during this project period. Our first literature report in this area was highlighted as the issue cover of *Inorganic Chemistry* in the May 29, 2006 edition. We demonstrated the original concept of low power photon upconversion (green-to-blue light) using MLCT sensitizers in conjunction with anthracene or diphenylanthracene triplet energy acceptors towards the end of the last reporting period which received substantial attention in the scientific community as described in the previous report. Since September of 2005, we have generalized this low power upconversion process to other metal complexes such as Ir(ppy)₃ (ppy is 2-phenylpyridine) and now includes other aromatic hydrocarbons such as pyrene. We have also developed a straightforward quantitative method for the actinometric determination of absolute upconversion quantum yields which does not rely on standards, approximations, or assumptions using specially designed jacketed optical cells. Another important development since the last report is the extension of the low power upconversion process to sensitize the production of chemical products normally requiring the input of UV light. In other words, Ru(II) complexes excited with low power monochromatic visible light drives the dimerization of anthracene in acetonitrile solutions. Anthracene dimerization was selected as a prototypical cycloaddition reaction that traditionally requires UV light input and clearly illustrates our newly developed concept of upconversion photochemistry.

4. ACCOMPLISHMENTS/NEW FINDINGS

This proposal is primarily concerned with the design, synthesis, and photophysical characterization of photochemically stable metal-organic chromophores with low-lying triplet excited states, intended to possess systematically variable excited state absorption and emission properties. The main project theme is to investigate alternate pathways to populate long-lived excited triplet states of interest for Air Force applications including power limiting, ultrafast switching, remote identification, and solution-based photon upconversion processes. In many instances, metal-to-ligand charge transfer (MLCT) excited states are used to internally sensitize the formation of excited triplet states localized on the appended "organic" system with visible light. Progress has been made in all proposed project areas over the past year's funding period. We have prepared and structurally characterized a number of the originally proposed as well as newly designed Pt^{II} synthetic targets; these have the general structural formulae $\text{Pt}(\text{LL})(\text{CCR})_2$ and $[\text{Pt}(\text{LLL})(\text{CCR})]^+$ (LL is a single substituted bipyridine; LLL is a substituted terpyridine ligand; CCR represents various arylacetylides, oligo-alkylacetylides, or oligo-arylacetylides). These molecules are purposely designed to possess low energy charge transfer absorptions poised to sensitize the highly-absorbing triplet excited states on the pendant acetylide ligand(s). In other words these molecules are potential candidates for optical limiting based on reverse saturable absorption (RSA) and possibly two-photon absorption (TPA). The structures generated since the inception of this project (middle of 2005) through September 2006 are presented in Figure 1.

4A. PROGRESS IN Pt^{II} CHARGE TRANSFER CHROMOPHORES. Compound 3 featured in Figure 1, $[\text{Pt}(\text{dbbpy})(\text{tda})]$, represents a novel chromophore design incorporating a metallacyclyne motif which leads to an MLCT complex with enhanced photophysical properties. In CH_2Cl_2 , $\text{Pt}(\text{dbbpy})(\text{tda})$ exhibits a strong visible charge transfer absorption and broad emission centered at 562 nm, Figures 2 and 3. The photoluminescence quantum yield and excited state lifetime are 0.52 and 2.56 μs , respectively, at room temperature. These parameters indicate that the planarization and rigidity introduced by the cyclic diacetylide leads to a lower energy absorbing species displaying enhanced photophysics relative to the analogous $\text{Pt}(\text{dbbpy})(\text{C}\equiv\text{CPh})_2$, 1a. TD-DFT calculations which include solvation by CH_2Cl_2 via the polarizable continuum model were used to

reveal the nature of the excited states in these molecules that are responsible for the charge transfer transitions. The 77 K emission spectra of the two compounds in EtOH/MeOH glasses were directly compared, uncovering tda-based ligand-localized phosphorescence in **3** at low temperature, Figure 4. Both the RT and 77 K emission spectra are directly compared to that of the model compound Pt(dppp)tda [dppp = 1,3-bis(diphenylphosphino)propane] (**4**), which features the Pt-perturbed



4

tta chromophore but lacks low-lying charge transfer excited states. Therefore, this molecule serves to approximate the ligand-localized triplet state in **3**. These results suggest that with the

proper selection of cyclyne, it may be possible to observe room temperature triplet state photophysics confined to the diacetylide subunit in related structures that are sensitized using the

visible absorbing MLCT manifold. This work was featured as the cover story in the May 29, 2006 issue of *Inorganic Chemistry*, see image to the right.

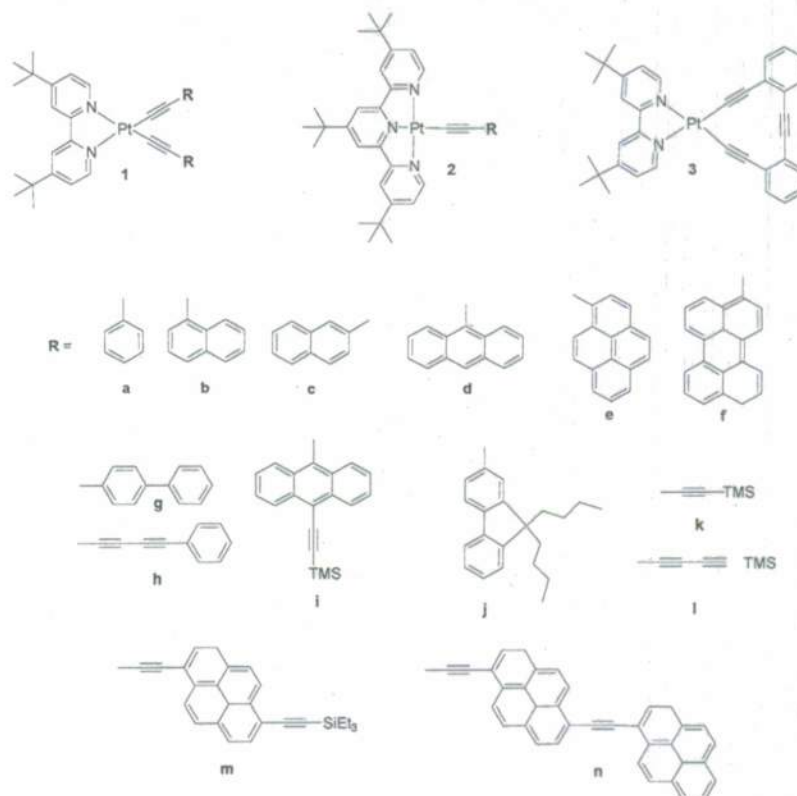
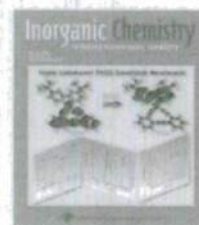


Figure 1. Chemical structures of the Pt(II) complexes and ligand sets synthesized to date.

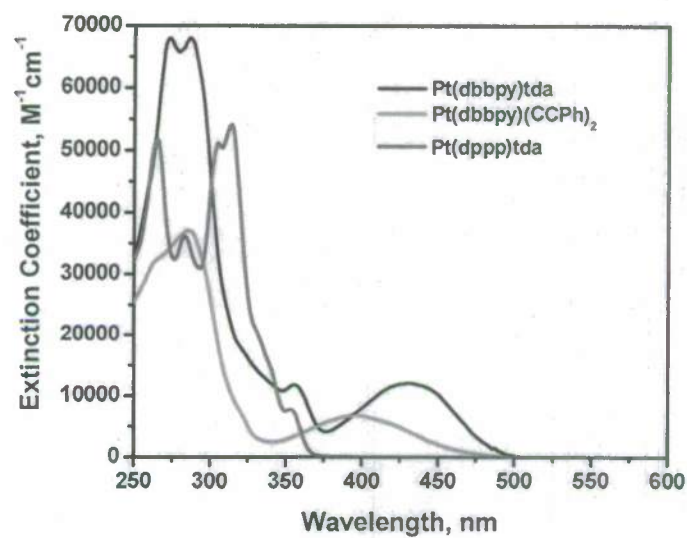


Figure 2. UV-Vis absorption spectra of **1a**, **3**, and **4** in CH_2Cl_2 .

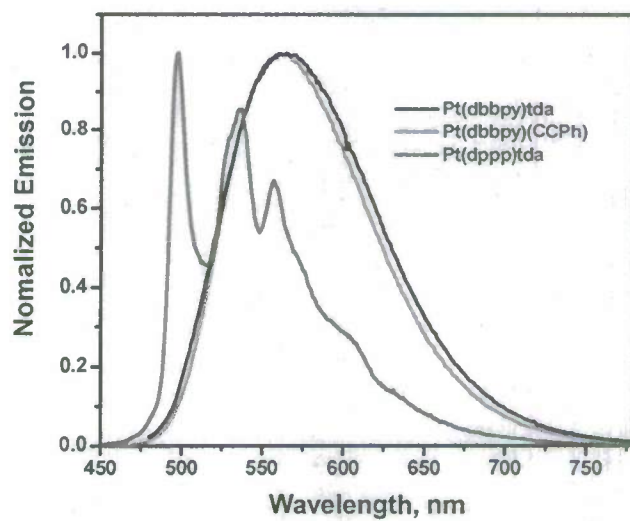


Figure 3. Static photoluminescence spectra of **1a**, **3**, and **4** in deaerated CH_2Cl_2 .

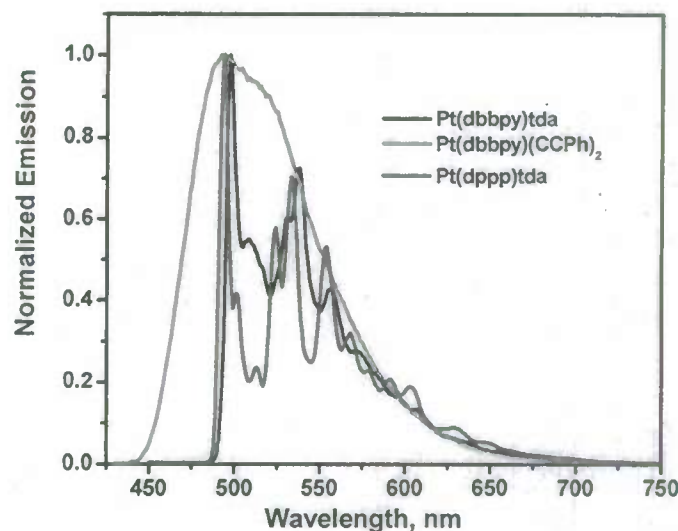


Figure 4. Static photoluminescence spectra of **1a**, **3**, and **4** in 4:1 EtOH/MeOH glasses at 77 K.

A comprehensive photophysical study was performed over the past year of funding which compared the ground and excited state properties of four platinum(II) terpyridyl acetylide compounds of the general formula $[\text{Pt}(\text{'Bu}_3\text{tpy})(\text{C}\equiv\text{CR})]^+$, where $\text{'Bu}_3\text{tpy}$ is 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine, having meaningful differences in molecular structure, Figure 5. The single crystal X-ray structure of one of these chromophores, $[\text{Pt}(\text{'Bu}_3\text{tpy})(\text{C}\equiv\text{CSiEt}_3)]\text{BF}_4$, was also determined during the course of this study. To further aid spectroscopic assignments, $[\text{Ru}(\text{'Bu}_3\text{tpy})_3]^{2+}$ and the pivotal synthetic precursor $[\text{Pt}(\text{'Bu}_3\text{tpy})\text{Cl}]^+$ were also investigated in this work. The latter two complexes possess short excited state lifetimes and were investigated using ultrafast spectrometry while the other four compounds were evaluated using conventional nanosecond transient absorption spectroscopy. The original intention of this study was to comprehend the nature of the impressive excited state absorptions that emanate from this class of transition metal chromophores. Consistent with previous observations, the ground state absorption and photoluminescence properties in this class of molecules are coarsely tuned with variation in the acetylide subunit, Figures 6 and 7. At the same time, the excited state absorption difference spectra across the series contain the same salient features which are modulated only slightly in wavelength and markedly in intensity as a

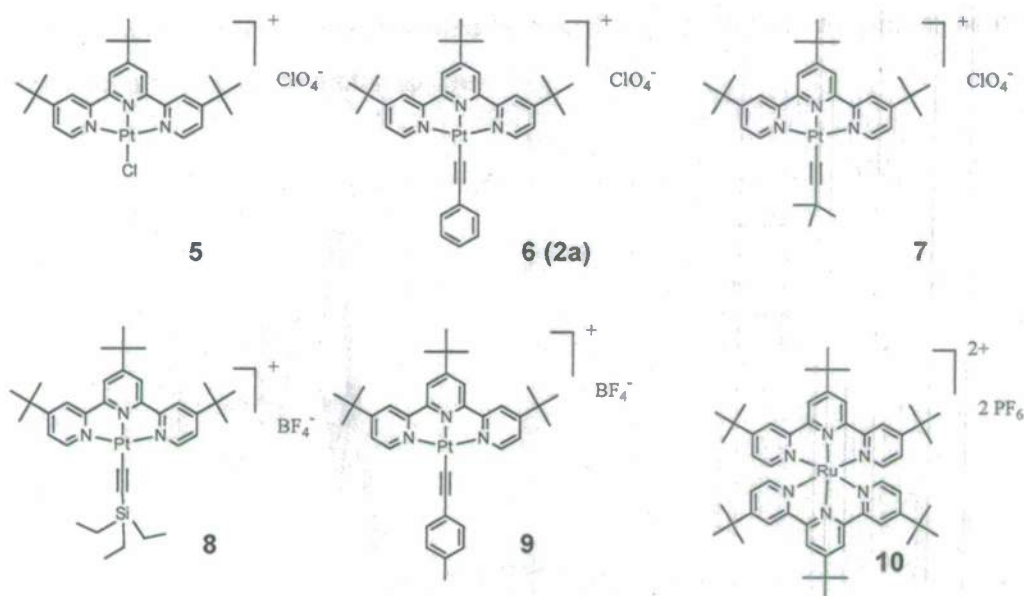


Figure 5. Chemical structures some platinum(II) terpyridyl acetylides along with relevant model chromophores.

function of appended acetylide ligand. More intense absorption transients are observed in the arylacetylide structures relative to those bearing an alkylacetylide, consistent with transitions coupled to the π system of the ancillary ligand, Figure 8. One electron reductive spectroelectrochemical measurements successfully generated the electronic spectrum of the $^1\text{Bu}_3\text{tpy}$ radical anion in all six complexes at room temperature. In the five Pt(II) molecules, the spectroelectrochemical data are quantitatively similar as one would anticipate given the consistency in their structures. These data also bear some resemblance to that exhibited in the one-electron reduction of the Ru(II) complex. The absorptions associated with the $^1\text{Bu}_3\text{tpy}$ radical anion simply do not account for intense optical transitions observed in the excited state of the Pt(II) chromophores. Transient trapping experiments using the spectroscopically silent reductive quencher DABCO clearly demonstrate the loss of most transient absorption features in the acetylide complexes throughout the UV, visible, and near-IR following bimolecular excited state electron transfer. The excited state absorptions are therefore strongly tied to the photo-generated hole which is delocalized across the Pt center and the ancillary acetylide ligand. Unfortunately, the instability of these complexes towards one-electron oxidation prohibits an exact assignment of whether the excited state absorptions result from

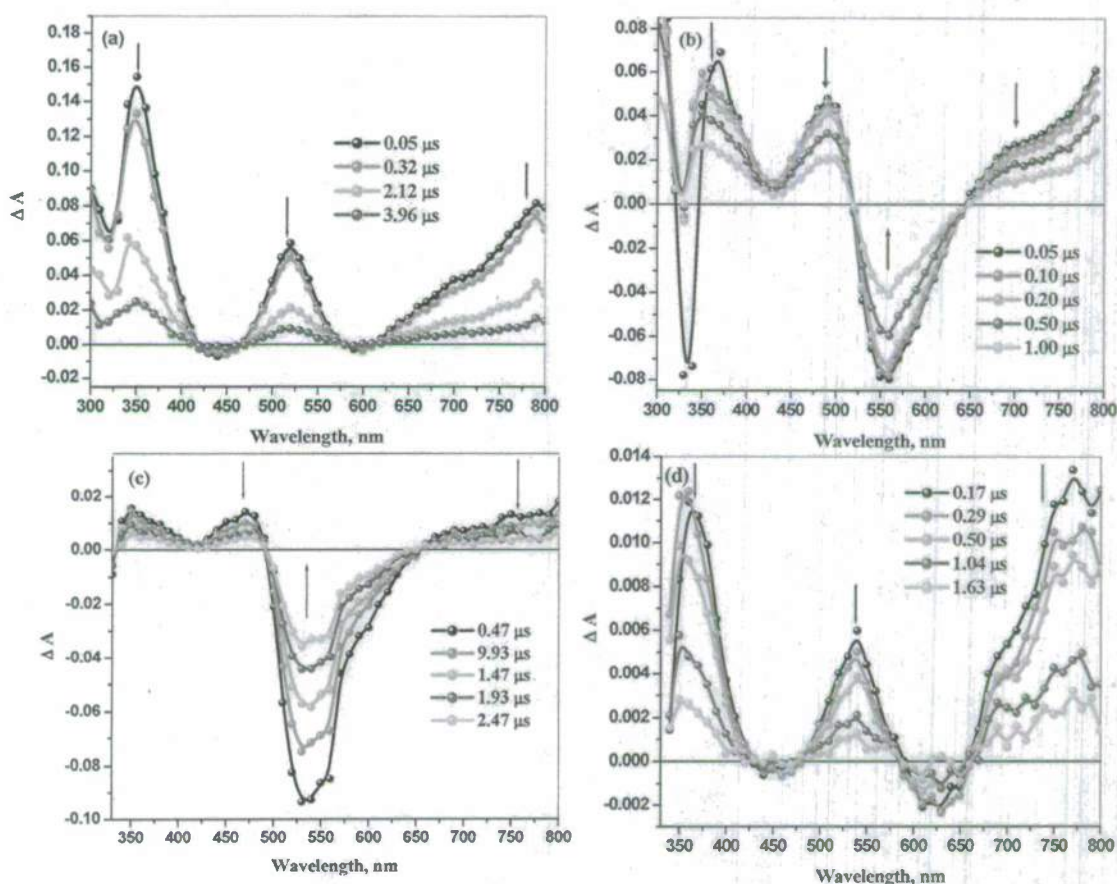
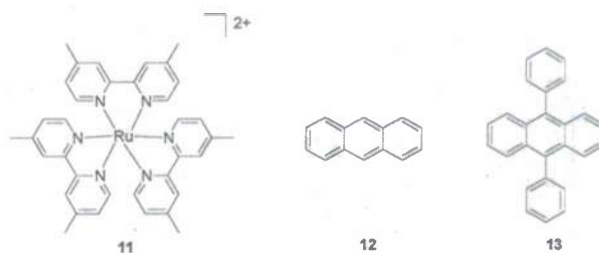


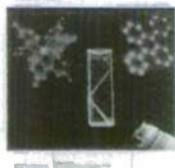
Figure 8. Transient absorption difference spectra of (a) **6**, (b) **7**, (c) **8**, and (d) **9** measured in CH_2Cl_2 following a 3 mJ, 355 nm laser pulse. The delay times are specified on each graph. The strong transient bleaches observed in (b) and (c) result from sample photoluminescence.

4B. PROGRESS IN PHOTON UPCONVERSION. To briefly summarize our progress to date, selective low energy excitation of the metal-to-ligand charge transfer (MLCT) transition in $[\text{Ru}(\text{dmb})_3]^{2+}$ ($\text{dmb} = 4,4'$ -dimethyl-2,2'-bipyridine) (**11**) in the presence of anthracene (**12**) or 9,10-diphenylanthracene (**13**) yields easily visualized upconverted singlet fluorescence resulting from triplet-triplet annihilation at low excitation power. The process is briefly described here to serve as an introduction to how our work has evolved since the last report. Our annihilation strategy permits the harnessing of sequential highly allowed one-photon absorptions to create higher energy excited states. In essence, the

energy stored in two separate excited triplet molecules is combined to generate a higher energy excited singlet state and a corresponding ground state species. In order to observe upconverted light in this scenario, the annihilating triplets must be sensitized using photons of significantly longer wavelength than those required to afford direct excitation of the singlet state. The originally proposed idea suggested that the judicious selection of an appropriate inorganic triplet sensitizer (where the intersystem crossing yield is unity) in concert with an aromatic hydrocarbon energy acceptor, may lead to efficient photon upconversion at low excitation power. The prototypical bimolecular triplet quenching (Eq. 1) and triplet-triplet annihilation (Eq. 2) reactions following low energy light excitation are given below using anthracene as the acceptors (An = anthracene):



A key feature of this sequence is the requirement to efficiently produce two sensitized **ChemComm** triplets in order to observe upconverted light emission from the anthracene singlet state. The utilization of the inorganic triplet sensitizer ensures quantitative production of triplet anthracene creating favorable conditions for annihilation (Eq. 2), process easily visualized at low excitation power (532 nm, < 5 mW) when optically dilute **11** is mixed with **13**, see image to the left.



An important question concerning photon upconversion in these light-producing reactions is how to properly gauge the efficiency of the process. The initial experiments

were optimized based largely on trial and error, using relative upconversion emission intensities as a guide. After several iterations, we designed an actinometric absolute quantum yield method which requires no approximations or corrections. Figure 9 presents a front-view (left) and side-on view (right) digital photographs of the jacketed optical cell used in the preliminary quantitative determinations.

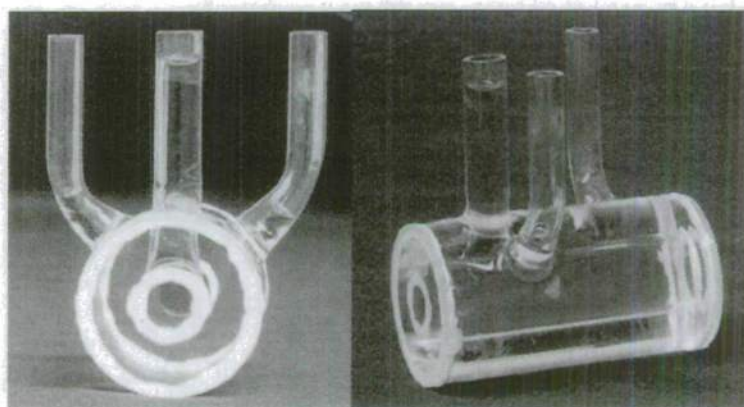


Figure 9. Jacketed optical cell used for the actinometric determination of absolute upconversion quantum efficiencies. A typical upconversion solution containing **11** and **13** are present in the inner optical cell while a ferrioxalate actinometer solution is present in the outer jacket.

The measurement of absolute quantum yield in this configuration is quite straightforward and note that a similar method has been used previously by other investigators attempting to measure normal fluorescence quantum yields (*J. Phys. Chem.* **1983**, 87, 83). Optical power meter readings incident and transmitted through the inner compartment permit calculation of the number of photons absorbed in the sample. Similarly, the emitted light produced by the inner solution is absorbed by the ferrioxalate solution, generating an Fe(II) concentration proportional to the number of emitted blue photons. The cell is wrapped in aluminum foil to prevent the leakage of upconverted photons. The Fe(II) concentration is determined as a function of time by monitoring the production of its highly colored tris(1,10-phenanthroline) complex, i.e. $[\text{Fe}(\text{phen})_3]^{2+}$. This information is then used to calculate the quantum yield for photon upconversion. The apparatus and experimental procedure was first evaluated using the conventional fluorescence from DPA (**13**) induced by 325 nm excitation from a HeCd laser. This value was within experimental error of that determined in the 1983 *J. Phys. Chem.* paper cited above

($\Phi_{\text{upconversion}} = 95\%$). Preliminary data obtained in the $[\text{Ru}(\text{dmb})_3]^{2+}$ /DPA system is presented in Figure 10, illustrating that the yield of upconversion varies as a function of DPA concentration, reaching a value of $\sim 7\%$ at 1 mM DPA, where the solution is near saturation in this acceptor/annihilator. We are presently improving our technique and are expanding the inventory of Ru(II) and aromatic hydrocarbon chromophores to be evaluated in absolute upconversion quantum yield determinations.

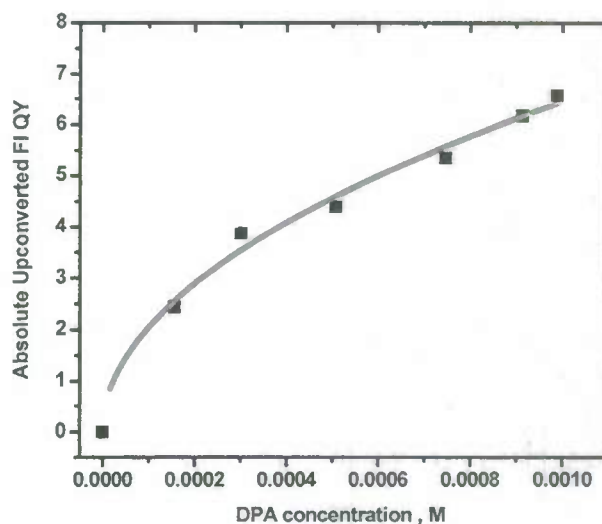


Figure 10. Absolute quantum efficiency of upconverted DPA fluorescence monitored as a function of DPA concentration in a deaerated CH_3CN solution containing $[\text{Ru}(\text{dmb})_3]^{2+}$ at $5.88 \times 10^{-6} \text{ M}$; $\lambda_{\text{exc}} = 457.9 \text{ nm}$; laser power = 46.0 mW.

Interested in extending the upconversion phenomenon towards the ultraviolet region of the electromagnetic spectrum, MLCT-sensitized upconverted fluorescence in non-covalent triplet energy transfer assemblies was investigated using $\text{Ir}(\text{ppy})_3$ as the sensitizer (ppy = 2-phenylpyridine) and pyrene or 3,8-di-*tert*-butylpyrene as the triplet acceptor/annihilator during this project period. Upconverted singlet fluorescence from pyrene or 3,8-di-*tert*-butylpyrene resulting from triplet-triplet annihilation (TTA) is observed following selective excitation of $\text{Ir}(\text{ppy})_3$ in deaerated dichloromethane solutions using 450 nm laser pulses. In both systems, the TTA process is confirmed by the near quadratic dependence of the upconverted fluorescence intensity on incident light

power, measured by integrating the upconverted delayed fluorescence kinetic traces as a function of incident excitation power. At the relatively high concentrations of pyrene that were utilized, pyrene excimer formation was detected by its characteristic broad emission centered near 470 nm. In essence, selective excitation of Ir(ppy)₃ ultimately resulted in the simultaneous sensitization of both singlet pyrene and pyrene excimers, the latter degrades the energy stored in the pyrene singlet excited state. Furthermore, in the case of di-*tert*-butylpyrene/Ir(ppy)₃, the formation of excimers is successfully blocked due to the presence of the sterically hindering *t*-butyl groups. This particular work demonstrates that sensitized TTA is indeed accessible to chromophore systems beyond those previously reported by our group (Ru(II) and anthracene based systems), suggesting the generality of the approach. We are currently exploring the possibility of upconversion using longer wavelength triplet sensitizers.

While the above advances have obvious relevance in photonic technologies, there are important preparative chemistry ramifications. If the TTA process is selected to produce reactive excited singlet species prone to cycloaddition chemistry, then low energy photons can be used to drive photochemical reactions traditionally requiring high energy ultraviolet light. This year we identified a representative synthetic application wherein the visible-light sensitized TTA upconversion efficiently drives bimolecular [4+4] cycloaddition chemistry between two anthracenes, accomplished through selective excitation of [Ru(dmb)₃]²⁺. The photodimerization of anthracene (An) is one of the oldest documented photochemical reactions, the nature of which has been extensively investigated by many researchers. Since we were interested in identifying a prototype addition reaction amenable to sensitized TTA using Ru^{II} metal-to-ligand charge transfer (MLCT) chromophores, An dimerization represented a suitable departure point.

Equations 1-3 provide the sequence of chemical steps necessary for the observation of photochemical upconversion in the current study. Note that Eqs. 1 and 2 are exactly the same as presented earlier in this report. Selective excitation of [Ru(dmb)₃]²⁺ using a variety of visible wavelengths (457.9 nm, 488 nm, 514.5 nm, or 532 nm) initiates bimolecular triplet-triplet quenching by An (Eq. 1). Two molecules of

excited triplet An ($^3\text{An}^*$) can encounter, ultimately resulting in TTA, Eq. 2. The dimer (An_2) is then produced from the interaction between an excited singlet An ($^1\text{An}^*$) and an An molecule in the ground state, thereby completing the photochemical upconversion reaction sequence, Eq. 3. It is important to note the photocatalytic nature of the Ru^{II} sensitizer whose ground state is regenerated following triplet energy transfer, Eq. 1. Given the inherent photochemical and thermal stability of Ru^{II} *tris*(diimine) complexes, one would expect long term efficacy and large turnovers in preparative synthetic applications using these chromophores in concert with sensitized photochemical upconversion.



Figure 11 provides representative static UV-Vis absorption data obtained from low power Ar^+ laser photolysis ($\lambda_{\text{ex}} = 457.9 \text{ nm}$) of a vacuum degassed CH_3CN solution containing $[\text{Ru}(\text{dmb})_3]^{2+}$ and An under relatively dilute concentrations. Selective excitation of the Ru^{II} chromophore leads to the net loss of An as a function of photolysis time. This is conveniently monitored by changes in the characteristic An vibronic absorption bands between 325-375 nm. After 70 min of photolysis the reaction is nearly complete with the low energy MLCT absorption bands remaining essentially intact. The quantum yields of An dimerization were measured as a function of An concentration while maintaining constant sensitizer concentration and incident laser power, Figure 12. The dimerization quantum yields sharply increase from 0 to 2.5% between 0 and 3 mM and then slowly rise, ultimately reaching 3.75% at 14 mM in CH_3CN , the highest concentration used in this experiment. At low An concentration, the steep slope in Figure 12 likely results from more efficient production of $^3\text{An}^*$, as suggested by Stern-Volmer analysis of the initial quenching step. At higher An concentrations, the dimerization quantum yield continues to increase linearly with concentration, consistent with a dimerization process under strict kinetic control by ground state An molecules. This finding, coupled with the pseudo-first-order nature of the photolysis data in Figure 11,

strongly suggests that the An which reacts in Eq. 3, is not the geminate An ground state molecule produced from annihilation in Eq. 2. A limitation of the annihilation approach lies in the fact that it relies on long-lived excited triplets to produce excited singlet molecules. This inherently limits the quantum yield of excited singlet state formation resulting from TTA encounters to a maximum value of 1/9 (11.1%), based upon spin statistics. Of course, if the quantum yield for the relevant singlet state reaction is below unity, the analogous TTA-controlled process will scale downward accordingly, as it likely does in the present work. In the case of An, it is known that higher ground state concentrations facilitate quenching of $^3\text{An}^*$ which diminishes the $^3\text{An}^*$ lifetime and concentration, leading to fewer annihilation events. Based on these facts, it can be anticipated that further increasing the An concentration much beyond that employed in the current work will likely lead to diminished dimerization yields in photochemical upconversion. However, even with consideration of these limitations, millimolar An concentrations are indeed suitable for synthetic chemistry utilizing upconversion phenomena.

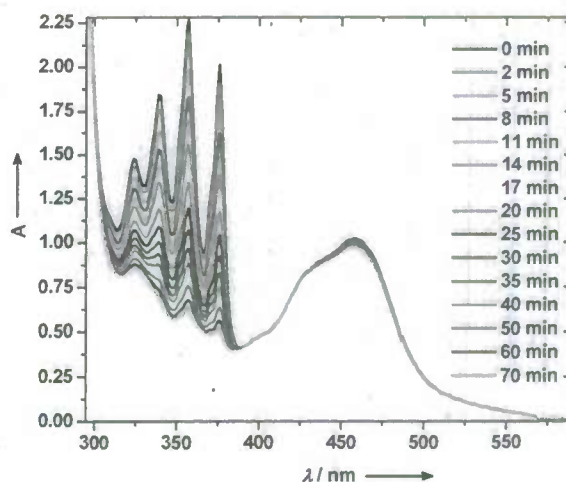


Figure 11. Photolysis of an acetonitrile solution of $[\text{Ru}(\text{dmb})_3]^{2+}$ ($5.75 \times 10^{-5} \text{ M}$) and anthracene ($2.55 \times 10^{-4} \text{ M}$) using continuous wave Ar^+ laser excitation, $\lambda_{\text{exc}} = 457.9 \text{ nm}$, at an incident power of 13.0 mW.

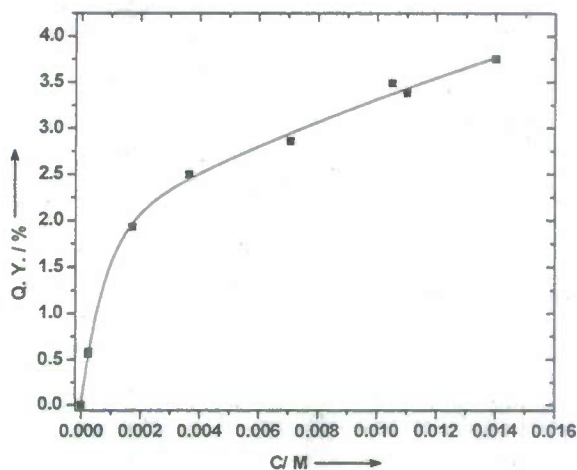


Figure 12. Dependence of anthracene photodimerization quantum yield on anthracene concentration. Acetonitrile solutions of $[\text{Ru}(\text{dmb})_3]^{2+}$ (5.75×10^{-5} M) and anthracene were irradiated with an Ar^+ laser, $\lambda_{\text{exc}} = 457.9$ nm, 13.0 mW.

Photodimer formation is clearly observed in the deaerated CH_3CN solutions as the nonpolar dimer readily crystallizes during the course of the photolysis. Digital photographs taken after 40 minutes of visible light irradiation, Figure 13, illustrate the extent of reaction and the ease at which sensitized photochemical upconversion takes place.

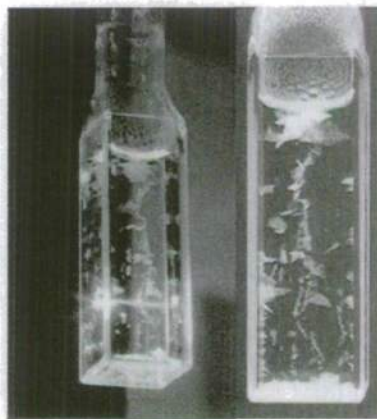


Figure 13. Digital photographs illustrating the "photochemical upconversion" concept in a solution with crystallized anthracene photodimer produced by Ar^+ laser photolysis of an acetonitrile solution containing $[\text{Ru}(\text{dmb})_3]^{2+}$ (5.25×10^{-5} M) and anthracene ($\sim 1.4 \times 10^{-2}$ M); laser on (left), laser off (right).

This latter work establishes the feasibility of applying sensitized TTA in preparative chemistry using anthracene dimerization as a prototypical reaction. The extension of this concept to other intermolecular cycloaddition reactions, including mixed dimers, represents research activity that will undoubtedly yield new insight into how TTA-driven reactions influence product distributions. In terms of materials science applications, TTA may provide a means to running desired chemical reactions in media that do not permit transmission of ultraviolet light.

5. PERSONNEL ASSOCIATED WITH THE PROJECT (9/1/05 – 8/31/06)

Felix N. Castellano: Professor of Chemistry, PI

Evgene O. Danilov: Research Assistant Professor, Ohio Laboratory for Kinetic Spectrometry

Wei Zhao: Postdoctoral Associate (since September 2005)

Radiy R. Islangulov: Graduate Assistant

Elena Shikhova: Graduate Assistant

Maria L. Muro: Graduate Assistant

Fei Hua: Graduate Assistant

Petr Ledin: Undergraduate Assistant (June 2006 – August 2006)

6. PEER-REVIEWED PUBLICATIONS (9/1/05 – 8/31/06)

Luminescent Charge Transfer Platinum(II) Metallacycles. Hua, F.; Kinayyigit, S.; Cable, J.R.; Kirschbaum, K.; Pinkerton, A.A.; Castellano, F.N., *Inorg. Chem.* **2006**, submitted.

The Nature of the Lowest Excited State in Platinum(II) Terpyridyl Acetylide Complexes. Shikhova, E.; Danilov, E.O.; Kinayyigit, S.; Pomestchenko, I.E.; Ziessel, R.; Castellano, F.N. *Inorg. Chem.* **2006**, submitted.

Upconverted Emission from Pyrene and Di-tert-butylpyrene using Ir(ppy)₃ as Triplet Sensitizer. Zhao, W.; Castellano, F.N. *J. Phys. Chem. A* **2006**, *110*, 11440-11445.

Photochemical Upconversion: Anthracene Dimerization Sensitized to Visible Light using Ru(II) Chromophores. Islangulov, R.R.; Castellano, F.N. *Angew. Chem. Int. Ed.* **2006**, *45*, 5957-5959; *Angew. Chem.* **2006**, *118*, 6103-6105.

Platinum(II) Diimine Diacetylides: Metallacyclization Enhances Photophysical Properties. Hua, F.; Kinayyigit, S.; Cable, J.R.; Castellano, F.N. *Inorg. Chem.* **2006**, *45*, 4304-4306. *Inorganic Chemistry* cover story, May 29, 2006 issue.

Photophysical Processes in Bipyridyl and Terpyridyl Platinum(II) Acetylides. Castellano, F.N.; Pomestchenko, I.E.; Shikhova, E.; Hua, F.; Muro, M.L.; Rajapakse, N. *Coord. Chem. Rev.* **2006**, *250*, 1819-1828.

Photo Processes on Self-Associated Cationic Porphyrins and Plastocyanin Complexes 1. Ligation of Plastocyanin Tyrosine-83 onto Metalloporphyrin and Electron Transfer Fluorescence Quenching. Anula, H.M.; Myshkin, E.; Guliaev, A.; Luman, C.R.; Danilov, E.O.; Castellano, F.N.; Bullerjahn, G.S.; Rodgers, M.A.J. *J. Phys. Chem. A* **2006**, *110*, 2545-2559.

Direct Interrogation of Triplet Intraligand Excited States using Nanosecond Step-Scan FT-IR. Polyansky, D.; Castellano, F.N. *Inorg. Chem.* **2006**, *45*, 2370-2372.

7. INTERACTIONS/TRANSITIONS (9/1/05 – 8/31/06)

(A) PRESENTATIONS AT MEETINGS, CONFERENCES, AND SEMINARS

Low Power Photoluminescence and Photochemical Upconversion. Castellano, F.N.; Islangulov, R.R. EDAI Gordon Conference, Newport, RI, August 2006.

Electron and Energy Transfer in Platinum(II) Polyimine Complexes Bearing Aryl- and Ferrocenylacetylde Units. Kinayyigit, S.; Kozlov, D.V.; Castellano, F.N. EDAI Gordon Conference, Newport, RI, August 2006.

Excited State Properties of Platinum(II) Terpyridyl Acetylides. Shikhova, E.; Pomestchenko, I. E.; Kinayyigit, S.; Danilov, E.O.; Castellano, F.N. EDAI Gordon Conference, Newport, RI, August 2006

Luminescent Charge Transfer Platinum(II) Metallacycles. Hua, F.; Kinayyigit, S.; Cable, J.R.; Kirschbaum, K.; Pinkerton, A.A.; Castellano, F.N. Inorganic Chemistry Gordon Conference, Newport, RI, July 2006.

Low Power Upconversion Using MLCT Sensitizers. Castellano, F. N. 231st American Chemical Society National Meeting, Atlanta, GA, March 2006 (INOR 674).

Platinum(II) Diimine Diacetylides: Metallacyclization Enhances Photophysical Properties. Hua, F.; Kinayyigit, S.; Cable, J. R. Castellano, F. N. 231st American Chemical Society National Meeting, Atlanta, GA, March 2006 (INOR 173).

Green Photoluminescence from Platinum(II) Complexes Bearing Silylacetylide Ligands. Hua, F.; Kinayyigit, S.; Cable, J. R. Castellano, F. N. 231st American Chemical Society National Meeting, Atlanta, GA, March 2006 (INOR 171).

Excited State Properties of Platinum(II) Terpyridyl Acetylides. Shikhova, E.; Pomestchenko, I. E.; Kinayyigit, S.; Danilov, E. O.; Castellano, F. N. 231st American Chemical Society National Meeting, Atlanta, GA, March 2006 (INOR 170).

A Bright Future for MLCT Excited States. Wright State University, Dayton, OH, September 23, 2005.

(B) CONSULTATIVE AND ADVISORY FUNCTIONS TO OTHER LABORATORIES AND AGENCIES

Over the course of the performance period we have had regular communication with scientists at the AFRL/MLPJ in Wright Patterson AFB by telephone, E-mail, as well as personal visits on my part to the AFRL and on their part to BGSU. The primary contacts at the AFRL include Joy Rogers, Thomas Cooper, and Daniel McLean. Prof. Kirk Schanze at the University of Florida (UF) and I have developed a collaborative effort where my group is investigating ultrafast processes in a variety of metal-organic chromophores developed at UF. These chromophores are at the heart of Schanze's current AFOSR funding. A similar relationship is beginning to develop with Prof. John Reynolds (also AFOSR supported) at UF as well. During the current project period, we also have developed a collaboration with Dr. Lin X. Chen at Argonne National Laboratory where she will apply time-resolved X-ray spectroscopy (visible pump/X-ray probe) to study solution structures and the associated dynamics of some Pt(II) chromophores that are central to the current AFOSR funding.

(C) TRANSITIONS

Over the course of the last one year funding period, the AFRL/MLPJ group has begun the investigation/testing of several of our Pt(II) compounds in their facilities with the intention of identifying promising samples for optical power limiting applications.

8. NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

The major scientific discovery during the past funding period was the realization of photochemical upconversion, using low energy visible photons to drive cycloaddition reactions traditionally requiring the input of UV light. Another development worth mentioning was the successful design, synthesis, and characterization of a new class of Pt(II) molecules based on metallacyclic diacetylide ligand structures. The first complex generated in this laboratory possesses photophysical properties that surpass all other molecules in its structural class.

9. HONORS/AWARDS

The PI currently holds the BGSU Olscamp Research Award (11/05 – 11/06) which is the institution's most prestigious award for research accomplishments. The PI was also early promoted to Full Professor during this year's funding period.